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Research Paper

Monitoring of Pesticide Residues in Different Agriculture Fields Effect of Different Home Processes on the Pesticides Elimination

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Abstract: *The effect of washing, storing, boiling, peeling, cooking with and without vinegar and frying on pesticide residue were investigated for vegetables and water/soil samples collected from Aga-Dhakahlia (Field 1), Nobaria, Behera (Field 2) and Giza (Field 3). Residues of organophosphorus, carbamate, organochlorine, fungicide, pyrethroid and abamectin pesticides.in the processed were analysed by gas and HPLC chromatography. Statistical analysis showed that potatoes contained the highest levels of dimethoate and diazinon as organophosphorus pesticides. Residue of pirimiphos-methyl in green bean and potatoes and residues of methomyl, abamectin and dicofol in cucumber and tomatoes were found to be were higher than their corresponding MRL's. Effect of some common food processing techniques (simple washing combined with cooking and/or frying techniques and drying of green bean) were also investigated and the results reported their effectiveness in residues reduction. It was found that, washing process eliminated approximately 13-60% of organophosphorus, 20-50% of carbamates, 19-25% of cypermethrin, 60% of dicofol, 100% of penconazole and 18-75% of abamectin residues. Peeling of washed cucumber removed 65% of malathion, 66% of methomyl, 80% of dicofol and 83% of abamectin. It might be concluded that a combination of simple washing and peeling removed 10 to 85% of insecticides if applied before consumption. As well, cooking and frying might help to remove 25-100% of the residual insecticides. Irrigation and drainage water were contaminated with pesticides such as malathion, dimethoate, methomyl, aldicarb, dicofol and abamectin. Effect of storage on the abamectin found with vegetables and soil after spraying suggested that the residue of abamectin was gradually decreased with storage time. Final recommendations for this study is that monitoring programmes of pesticide residues in local produces must be expanded to include all food items and potentially harmful pesticide residues in order to generate information and establishing data based on food contaminants.*

Keywords: Pesticides residues, home processing, soil, irrigation water, drainage water.

Introduction

Pesticides used in agriculture is necessary in the production of food. Indeed, they are widely used to control crop pests. The use of high persistent organochlorine insecticides was curtailed since 1989s. A low persistence organophosphate, carbamate, synthetic pyrethroid and other pesticides that have currently been used against pests of most vegetables and fruit crops had replaced them. During the last decade, several surveys on fruits and vegetables with pesticides were reported [1-4]. However, the health risk associated with breakdown products must be considered since pesticide breakdown products might also be hazardous, as illustrated by the formation of the suspected carcinogen ethylene thiourea from ethylene bisdithiocarbamate fungicides [5, 6]. It is well known that processing food can affect the level of pesticide residues. Food and health authorities around the world were continuously monitoring pesticide residues in fruit and vegetables. Dietary risk assessment can be refined by taking into consideration changes in pesticide residues during industrial and home processing [7]. Typical home processing includes washing, boiling, peeling and juicing of fruit and vegetables. The effects of processing on pesticide residues in food compiled in reviews [8-10]. The

Equipments

High performance liquid chromatograph (HPLC) instrument was used for analysis of some pesticides. It was of the type Perkin Elmer series 410 LC Pump Chromatograph, with ALC 95 UV/visible spectorphotometer detector and C_{18} stainless column. Methanol/ Acetonitrile (80/20) was used as mobile phase at a flow rate of 1 ml / min. Duplicate injection of 2 ul were used for standard solution and for sample injection.

A Hewlett gas liquid chromatograph model 5890 instrument, equipped with flame ionization detector (FID), coupled with 3392 A-HP integrator was used. Ph. ME silicon (HP- 50 cross linked 50% on 80-100 mesh chromosorb W.H.P, column (1.5 ml x 0.53 nm i.d) was used. A Hewlett – Packard serial 6890 gas chromatograply, equipped with a ECD, the column was DB-17, 30 M× 0.32 Mm x 0.52 Mm film thickness. Drying oven (Techno group), laboratory balance (Sartorius AG Gottingen TE 2145, Germany), blender, electrical shaker (Tarco), rotary evaporator (Heidolph glass set Gl, Germany) and assorted glassware: volumetric flasks, conical containers, measuring cylinders, glass column, digestion tubs and separatory funnels of various capacities, were used.

Pesticide residue determination from samples

Extraction of pesticides: According to Luke et al [12] vegetable or fruit samples (20 g) were blended using high speed blender, 20 g of soil and 60 ml of acetone were added. The mixture was shaken mechanically using an electrical shaker for one hour, then filtered and rinsed twice with 25 ml acetone. The filtrate was transferred to a separatory funnel and a mixture of 1:1 petroleum ether: methylene chloride (120 ml) was added and shaked vigorously for 2 minutes. For separation, the upper organic layer was received through anhydrous sodium sulfate and lower aqueous layer was similarly extracted two more times with methylene chloride only. The combined methylene chloride extract was evaporated at 40 ^{o}C under reduced pressure using rotary evaporator. The residue was quantitatively transferred into small vials with 5 ml of methanol. The vials were stored for the cleanup procedure described by **AOAC** [13]. GLC and HPLC measurements were carried out under optimum condition [13].

The extraction technique mentioned by Mallhof [14] was adopted for the extraction of the pesticides under study as follows: 20 g of plant or soil was mixed with 60 ml of methanol. The mixture was shaked mechanically using an electrical shaker for one hour for separation of water from methanol extract. The extract was partitioned successively with 50, 25 and 25 ml of methylene chloride in separatory funnel after adding 25 ml of saturated NaCl solution. The combined methylene chloride phase was dried by filteration through filter paper and anhydrous sodium sulphate, then evaporated just to dryness on rotary evaporator at 40 ^{o}C. The pesticide residues were kept under refrigeration until starting the clean up procedure. The residue of imidacloprid processes acting on pesticide residues in the field such as volatilization, hydrolysis, oxidation, metabolism and enzymatic transformation are relevant for reduction of pesticide residues during processing [10].

It is well known that no monitoring study can determine all pesticides in fruits and vegetables, which would be economically unrealistic and practically impossible. So, the objective of the present study was to find out the extent and magnitude of certain group of pesticides residues in common vegetables. Also, to obtain data on how typical home-processing practices affect pesticide residues in tomatoes, cucumber, green bean and potatoes. The data would help in assessing the risk of human exposure to pesticides.

Material and Methods

The pesticides were from the following groups: organophosphorus [pirimiphos-methyl, suppliers Zeneca (98%), malathion, suppliers Cheminova (99%), dimethoate, suppliers Mico (96.1%), diazinon, suppliers Novartis (96%), profenofos, suppliers Novartis (92%)], carbamate [methomyl, suppliers Aventis (98%), (Aldicarb, suppliers Aventis (99.5%), carbofuran, supplier Bayer (98%)], neonicatinoid [imidacloprid, suppliers Bayer (98.5%)], organochlorine [dicofol, suppliers Lainco (99.7%)], avermectin [abamectin, suppliers Novartis (95%)], triazole [penconazole, suppliers Novartis (99.5%)] and pyrethroid [cypermethrin, suppliers Amico (99.5%)].

These compounds were identified by the Ministry of Agriculture and Land Reclamation recommendation No.663/1998. All the solvents and reagents used in this study were of high analytical and HPLC grade. Methanol (Merck 99.80%), acetone (Merck 99.90%), acetonitrile (BDH 99.9%) and n-hexane, methylene chloride, benzene, and petroleum ether were supplied from ADWIC. Anhydrous sodium sulphate and Florisil 60-100 mesh from Merck. Sodium chloride solution (10%), nitric acid (68%) were supplied from Panreac and perchloric acid (60%) was from Merck.

Sampling

The samples studied represent items most commonly consumed in an Egyptian diet according to the data obtained from the Nutrition Institute, Ministry of Health. Samples of 5 kg were subjected to home preparation techniques including cooking, washing and peeling before analysis to determine their effect on residue levels. Samples were obtained from Aga-Dhakahlia governorate (Cucumber, tomato, potatoes and green bean), El.Banger section Nobaria, Behera (Potatoes and tomato) and Giza–land (green house, cucumber) from June 2004 to June 2005 for qualitative and quantitative analysis of pesticides. Collection was divided into 2 periods, summer and winter period. General sample preparation steps adopted for each were according to the (FAO/ WHO) [11, 12] procedures.

2004 to June 2005.

pirimiphos-methyl

PMM is widely used to control pests in field crops as well as in vegetables. The main losses of the insecticide from treated surface are due to evaporation. In water, pirimiphos-methyl retains its toxicity from 6 to 11 weeks, vanishing from this medium as a result of evaporation and photolysis. In the soil, the insecticide migrates poorly, its half life in various soils fluctuating within four weeks. Table (2) and Figure (1) indicated that pirimiphos-methyl is non detectable in cucumber and tomatoes samples collected from fields 1, 2 and 3. However, the results show concentrations of pirimiphos-methyl of 2.76, 6.92, 3.57 and 0.62 ppm in green bean, potatoes, soil and irrigation water, respectively, collected from field (1).

The maximum residue limits (MRL's) of pirimiphos-methyl in green bean and potato plants (Table 3) are 0.50 and 0.05 ppm, respectively. It is clear that residues in green bean and potatoes are higher than their corresponding MRL's and thus indicating that it required a longer post harvest period for safe consumption. The results are in accordance with the information published by different countries (Canada, Finland, Denmark, Netherlands and USA) where cereals and their products, followed by potatoes and other vegetables are among the largest contamination [17].

Profenofos: Data listed in Table (2) and represented in Figure (1) indicated that, profenofos is non-detectable in cucumber, tomatoes, green bean and potatoes samples collected from field 2 and 3. While, concentrations of profenofos are 0.25 and 0.73 ppm in tomatoes and irrigation water, respectively, for samples collected from field (1). As the maximum residue limits, MRL's for profenofos was 2 ppm in tomatoes, the residues determined herewith are lower than their corresponding values. This is in harmony with those previously obtained [18]. These results also agree with the previous reported data that found that profenofos residues had persisted in garlic, strawberries and tomatoes for up to 3 weeks after the second application of profenofos and are quite comparable with those reported by *Shady et al* [19].

(ICP) and aldicarb (AC) after clean up were analysed by HPLC. The conditions for determination using HPLC are optimized.

The residues of penconazole were analyzed using GLC employing C_{18} column under the experimental conditions [15]. While, the residues of carbofuran and methomyl were analyzed using HPLC after the clean up procedure [16]. Residue level of abamectin (AM) in samples was determined by HPLC.

Results and Discussion

Several studies had shown that some pesticides decomposes completely into harmful substance fairly soon after they were exposed to environmental conditions such as air, water, sun light and high temperature. However, scientific conformation seems to be not fully understood. Pesticides remain in or on plants or soil or water, in very small amounts of parent compounds or their breakdown product, may be harmful and sometimes persist for a long time. The maximum residues in food should implement in the field of pesticides at an international level. The structures of the different pesticides used in this study are given in Scheme 1.

Recovery studies of pesticides

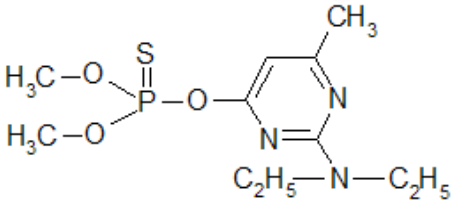
Under the optimum conditions, untreated samples of cucumber, tomatoes, green bean, potatoes and soil are spiked with known amount of pirimiphos-methyl, malathion, profenofos, dimethoate and diazinon, imidacloprid, aldicarb, methomyl, carbofuran and abamectin prior to extraction and cleaned up for recovery test of each pesticide. These samples are passed through the entire process of extraction then clean up and analyzed as previously described. Following such techniques, the recovery for the residues of the pesticides under investigation from spiked control samples are tabulated in Table (1).

Organophosphorus insecticides

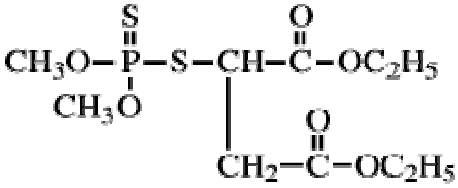
Organophosphorus residues are detected in all samples collected from different fields: - field (1) Aga, Missouri, field (2) El-Nobaria Behera and field (3) Dock Gaza (green house) during the period of study from June

Table 1
Percentage recovery of pesticides

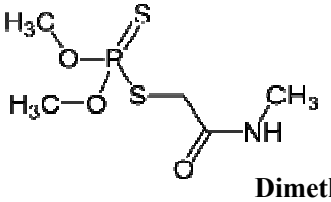
Compounds / Samples	% recovery									
	pirimiphos-methyl	malathion	profenofos	diazinon	dimethoate	imidacloprid	aldicarb	methomyl	carbofuran	abamectin
Cucumber	91.30	89.70	78.50	92.40	82.30	80.17	93.30	88.50	92.82	81.50
Tomatoes	97.70	98.80	86.30	75.90	91.86	91.15	87.07	91.60	85.05	95.40
Green bean	84.32	86.50	83.50	79.44	97.30	96.56	82.43	80.60	79.60	82.70
Potatoes	95.80	78.01	96.30	100.0	95.00	99.45	96.73	93.60	85.05	76.80
Soil	77.80	95.50	91.60	101.1	101.30	78.75	105.1	102.7	79.60	81.50



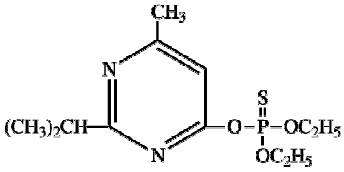
Pirimiphos-methyl



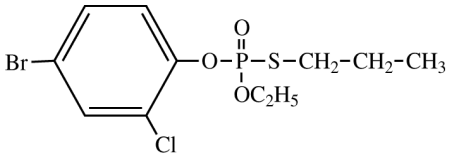
Malathion



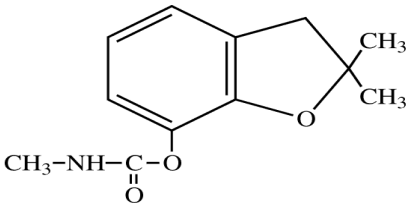
Dimethoate



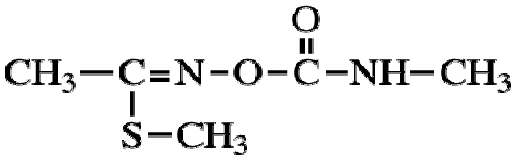
Diazinon



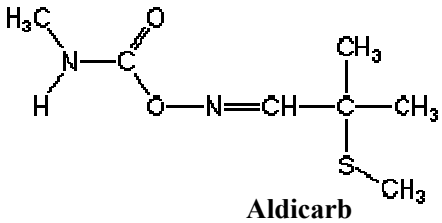
Profenofos



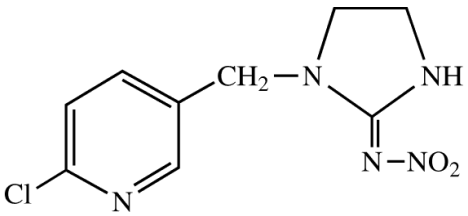
Carbofuran



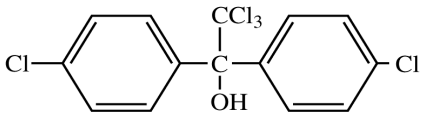
Methomyl



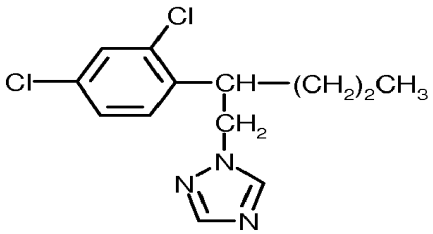
Aldicarb



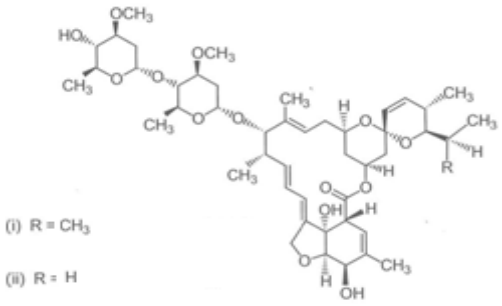
Imidacloprid



Dicofol



Penconazole



Abamectin

Scheme 1: Structures of different pesticides used

Table 2
Levels of pesticides residues (ppm) in vegetables, soil and irrigation water samples from different fields from 6-2004 to 6-2005

Samples	Fields	Pesticides	Mean* concentration (ppm)	SD	RSD(%)
Green bean	1	pirimiphos-methyl	2.76	0.023	1.30
Potatoes		pirimiphos-methyl carbofuran	6.92 0.81	0.03 0.03	1.45 1.50
Soil		pirimiphos-methyl aldicarb	3.57 7.00	0.03 0.03	1.64 1.90
Irrigation water		pirimiphos-methyl aldicarb profenofos	0.62 12.60 0.73	0.03 0.04 0.04	1.82 2.10 2.40
Tomatoes		profenofos	0.25	0.03	1.92
Potatoes		diazinon	4.97	0.03	1.70
Potatoes	2	malathion	0.62	0.02	1.27
Tomatoes		methomyl	3.23	0.02	1.2
Soil		malathion methomyl dimethoate	13.05 2.74 1.29	0.04 0.03 0.01	2.16 1.75 0.78
Irrigation water		malathion methomyl dimethoate	2.38 1.33 0.19	0.02 0.01 0.02	1.16 0.75 1.11
Potatoes 11-2004		dimethoate	1.28	0.02	0.93
Potatoes 2-2005		dimethoate	2.85	0.03	1.56
Soil		dimethoate	0.91	0.03	1.50
Irrigation water		dimethoate	0.26	0.04	2.16
Cucumber	3	malathion methomyl	0.83 8.17	0.02 0.02	1.06 1.00
Soil		malathion methomyl	0.78 10.85	0.02 0.02	0.84 0.90

* number of replicates = 3
Detection limit of pirimiphos-methyl = 1.5 ng
Detection limit of profenofos = 1ng
Detection limit of diazinon = 3ng
Detection limit of dimethoate = 5ng
Detection limit of malathion = 3ng.
Detection limit of carbofuran ≤ 0.01 ppm
Detection limit of aldicarb ≤ 0.01 ppm

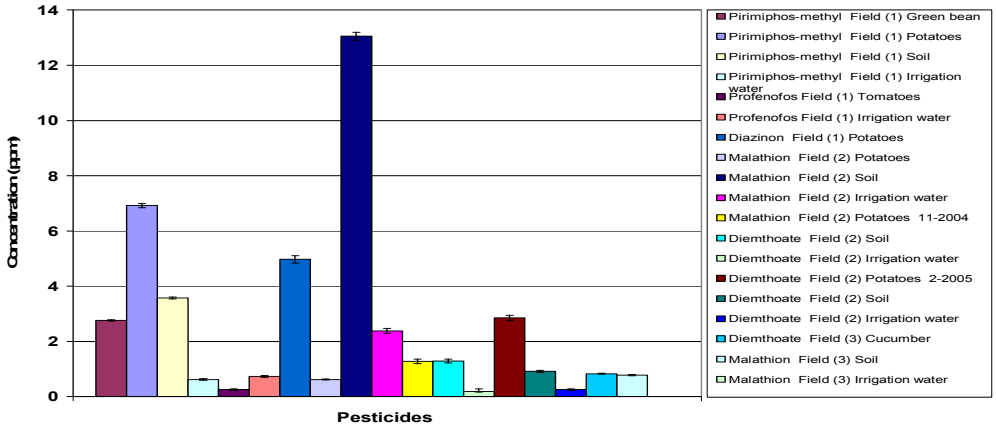


Figure 1: Levels Of Organophosphorus Residues (Ppm) In Vegetables, Soil And Irrigation Water Samples From Different Fields

Table 3
Tolerance level of insecticide in foods and drinking water

Samples / Pesticides	Cucumber	Tomatoes	Green bean	Potatoes	Water
Pirimiphos-methyl	1.00	1.00	0.50	0.05	0.10
Malathion	N.A	3.00	2.00	N.A	≈ 0.01
Profenofos	N.A	2.00	0.10	0.05	0.10
Diazinon	0.10	0.50	0.20	0.01	N.A
Dimethoate	N.A	1.00	N.A	0.05	N.A
Methomyl	0.20	0.50 , 0.10	2.00	0.10	0.05
Carbofuran	N.A	0.10	0.10 , 0.50	0.50	N.A
Aldicarb	N.A	N.A	N.A	N.A	N.A
Penconazol	N.A	N.A	N.A	N.A	N.A
Dicofol	2.00	1.00	2.00	N.A	N.A
Cypermethrin	0.20	0.50	0.50	N.A	N.A
Imidaclaprid	1.00	0.50	2.00	0.50	N.A
Abamectin	0.001	0.001	N.A	N.A	N.A

N.A. = non applicable.

Malathion: Malathion is widely used as organophosphorus pesticide due to its low persistence in the environment, low mammalian toxicity and high insecticidal activity. It has moderate toxicity but its crude and formulation contain impurities which are far more toxic to mammals. It was concluded from the results reported in Table (2) and Figure (1) that, malathion was found to be non detectable in tomatoes and green bean samples collected from fields 1, 2 and 3. As well as, these results also indicated that the concentrations of malathion of 0.62, 13.05 and 2.38 ppm were detected in potatoes, soil and irrigation water samples collected from field (2), respectively. However, the results show concentrations of malathion to be 0.83 ppm in cucumber and 0.78 ppm in soil collected from field (3). Similar results were reported by several investigators [20].

Dimethoate: It is obvious from the data listed in Table (2) and Figure (1) that dimethoate is non detectable in cucumber, tomatoes, green bean and potatoes samples collected from fields 1 and 3. While, its concentrations in potatoes, soil and irrigation water collected from field 2 were 1.28, 1.29 and 0.19 ppm in November (2004). But in February (2005), concentrations of dimethoate are found to be 2.85, 0.91 and 0.26 ppm, respectively. The MRL's for potato plants treated with dimethoate was 0.05 ppm (Table 3). However, residue in potatoes is found to be higher than their corresponding MRL's and thus, indicating that it required a longer post harvest period for safe consumption.

Diazinon: Diazinon was determined in different crops collected from different fields and the data are given in Table (2) and represented graphically in Figure (1). It indicates that diazinon was non detectable in cucumber, tomatoes, green bean and potatoes samples collected from field 2 and 3. As well, these results indicate that concentration of 4.97 ppm is detected in potatoes collected from field (1). It was reported that the MRL's for diazinon was 0.01 ppm in potatoes. However, residues in potatoes are higher than their corresponding MRL's. The low value of the calculated standard deviation (SD = 0.01 to 0.04) and relative standard deviation (RSD = 0.78 to 2.40) indicate the accuracy and precision of the.

Carbamate insecticides

Methomyl: The data presented in Table (2) show that the residues of methomyl are found to be non detectable in tested samples collected from field 1. While it is 8.17 ppm in cucumber and 10.85 ppm in soil samples collected from field 3. While the data reported also show that its residue in samples collected from field 2 is found to be 3.23, 2.78 and 1.33 ppm in tomatoes, soil and irrigation water, respectively. It was found that, the MRL's for cucumber and tomato plants treated with methomyl were 0.20 and 0.50 ppm, respectively. However, residues in cucumber and tomato are found to be higher than their corresponding MRL's and thus, indicating that, it requires a longer post harvest period for safe consumption. This result coincides with those previously reported [21]. Its residue levels are higher than allowed, an incidence ascribed to misuse and negligence. Also the degradation is very dependent on climate factors including sunlight and daily temperature fluctuations.

carbofuran

It was found that [22] found that carbofuran was preferred over many other insecticides because it had a low persistence in most soil types, breaks down in neutral or slightly alkaline water (half – life of 1 to 8 weeks) depending upon water temperature, does not bind to sediments or suspended particles, and does not bioaccumulate.

The concentration of carbofuran Table (2) is found to be 0.81 ppm in potatoes collected from field (1). No residues of it are detected in cucumber, tomatoes, potatoes, green bean, soil and irrigation water collected from both fields 2

and 3. The MRL's for carbofuran in potatoes is 0.5 ppm (Table 3). Thus, the results reported here with carbofuran residues in potatoes are higher than the respective allowed maximum residue limits. The rapid dissipation of the residues of the applied carbofuran from soil through few weeks could be attributed to the removal from the soil as a result of volatilization, evaporation, irrigation, downward movement, chemical and microbial degradation [21].

Aldicarb: It is obvious from the data reported in Table (2) that no residues of aldicarb are detected in cucumber, potatoes, tomatoes and green bean samples collected from different fields 1, 2 and 3. While, its concentration is found to be 12.60 ppm in irrigation water and 7.02 ppm in soil collected from field (1). Because it is very soluble in water, so that it move easily from soil into surface water or shallow ground water (ground water contamination). These results are in accordance with the findings previously reported [23].

Degradation of aldicarb started faster within the first 4 weeks followed by lower and gradual losses by the lapse of time. The low values of the calculated standard deviation (SD = 0.01 to 0.04) and relative standard deviation (RSD = 0.75 to 2.1) indicate the accuracy and precision of the methods utilized for determination of pesticides in the different vegetables, soil and irrigation water Table (2).

Organochlorine pesticide (Dicofol): In this work the studied vegetable samples are found to be free from any detectable amount of dicofol pesticide except tomatoes and cucumber. These data are in agreement with *Dogheim et al* [24].

Figure (2) shows that, the concentration of dicofol is non detectable in cucumber, tomatoes, green bean and potatoes samples collected from field 2 and 3. However, the results show concentrations to be 8.42 ppm in cucumber, 5.61 ppm in tomatoes, 22.60 ppm in soil and 3.49 ppm in irrigation water collected from field 1 (Table 4). The MRL's for cucumber and tomatoes plants treated with dicofol were 2 and 1 ppm, respectively. However in the present investigation, residues in cucumber and tomatoes are found to be higher than their corresponding MRL's. Dicofol residues are observed in soil samples collected from field (1). It indicates that dicofol was considered moderately persistent in soil, while (fungicide was reported to be moderately persistent in soil meanwhile) pyrethroid insecticide was of low persistence in soil environment.

Gonzales et al [25] stated that organochlorine pesticides were the most persistent and found to persist in field crop soils for long periods of time, with long half lives of disappearance ranging from 0.3–2.8 years in soil. The adsorption of the compounds by soil was influenced by divers factors such as organic matter content, soil type and physical-chemical properties of pesticides.

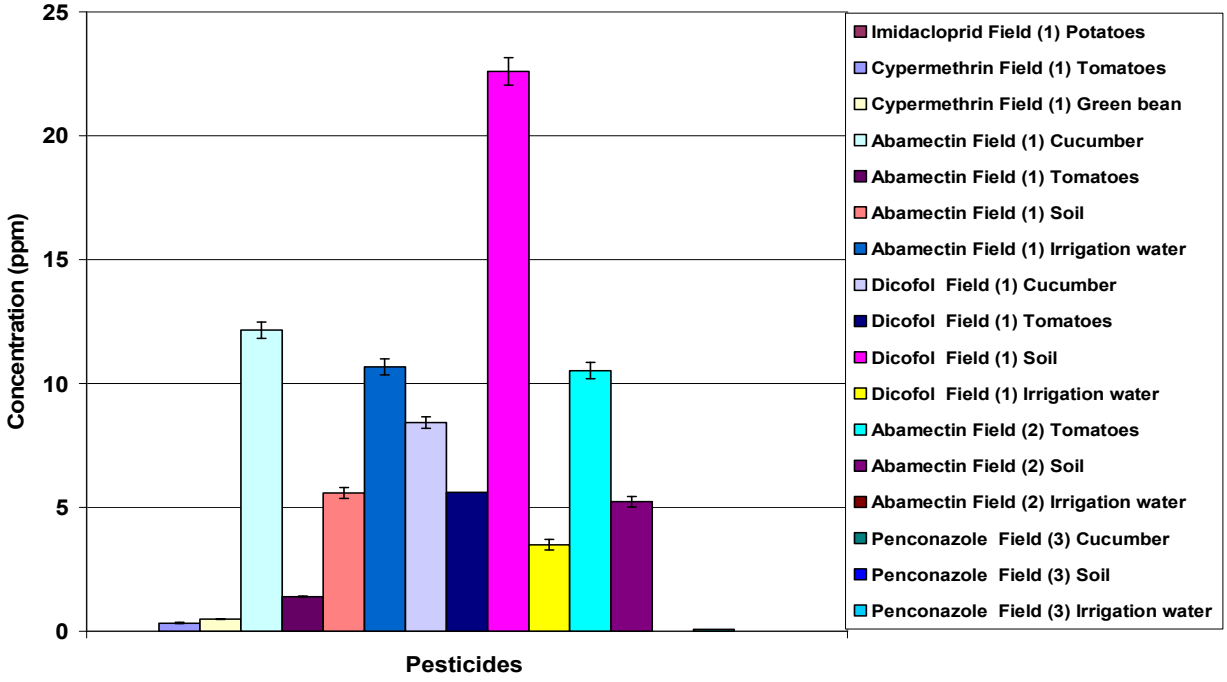


Figure 2: Levels of Imidacloprid, Cypermethrin, Abamectin, Dicofol and Penconazole (ppm) in vegetables, soil and irrigation water samples

Table 4
Levels of pesticide residues (ppm) in vegetables, soil and irrigation water samples from different fields (June 2004 – June 2005)

Samples	Fields	Pesticides	Mean* concentration	SD	RSD(%)
Tomatoes	1	cypermethrin	0.33	0.02	0.9
Green bean		cypermethrin	0.49	0.01	0.8
Cucumber		abamectin	12.16	0.02	1.41
Tomatoes		abamectin	1.40	0.02	1.23
Soil		abamectin	5.58	0.02	1.35
Irrigation water		abamectin	10.67	0.03	1.63
Cucumber		dicofol	8.42	0.03	1.53
Tomatoes		dicofol	5.61	0.02	1.32
Soil		dicofol	22.60	0.02	0.98
Irrigation water		dicofol	3.49	0.02	1.25
Tomatoes	2	abamectin	10.52	0.01	0.81
Soil		abamectin	5.23	0.02	0.96
Cucumber	3	penconazole	0.082	0.02	1.02

* number of replicates = 3 ; Detection limit of imidacloprid = < 0.01 ppm ; Detection limit of cypermethrin =1.5ng; Detection limit of abamectin = 0.005 ppm ; Detection limit of penconazole = 1.5ng; Detection limit of dicofol= 0.003 ppm

Pyrethroid insecticide (cypermethrin): Cypermethrin belongs to the class of pyrethroid insecticides, which were synthetic analogues of pyrethrins, the naturally occurring insecticidal compounds in the flowers. It was used as insecticide to control insect pests on crops. The results reported in Figure (2) suggest that cypermethrin is non detectable in cucumber, tomatoes, green bean, potatoes, soil and irrigation water samples collected from field 2 and 3. As well, these results (Table 4) indicate that the initial deposits of cypermethrin is found to be 0.33 ppm in tomatoes and 0.49 ppm in green bean samples collected from field (1). The MRL's for tomatoes was 0.5 ppm and for green bean was 0.5 ppm. Therefore, residue in tomatoes and green bean are lower than their corresponding MRL's.

Triazole pesticide (penconazole): The concentration of fungicide residue of penconazole Table (4) and Figure (2) is 0.082 ppm in cucumber samples collected from field (3). Likewise Lim et al [26] reported that the rapid disappearance of penconazole from the leaves was probably related to volatilization of penconazole.

Avermectin pesticide (abamectin): Data reported in Table (4) and Figure (2) demonstrate that the concentrations of abamectin is 12.16, 1.40, 5.58 and 10.67 ppm in cucumber, tomatoes, soil and irrigation water samples collected from field (1), respectively. While, its concentrations is found to be 10.52 and 5.23 in tomato and soil samples, respectively, collected from field 2. However, abamectin residue is non detected in field (3). Concerning health hazards, the MRL's for abamectin in cucumber and tomatoes was 0.001 ppm as related by codex alimentary committee for pesticide residues (Table 3). Therefore, its concentration in cucumber and tomatoes is found higher than the respective residue limits. Accordingly the pre-harvested intervals (PHI) were found to be 14 days for abamectin. This indicates that the crops could be safely marketed 14 days after treatment.

Neonicotinoid pesticide (Imidacloprid): Imidacloprid was one of new class of highly systemic chloronicotinyl insecticide with significant activity against a wide range of insecticides. It is found that imidacloprid is non detectable in cucumber, tomatoes, green bean, potatoes, soil and irrigation water collected from different fields.

Method for the removal of pesticide residues from vegetables: Typical home processing includes washing, boiling, peeling and frying of vegetables. The effect of processing on pesticide residues in food was complied in many reviews [27] covering a wide range of processing practices. The effect of processing practices on residues had been seen to vary with both crop and pesticides [28]. In general, it was important to use field-sprayed samples, since absorption, translocation and weathering of the pesticide might influence the effect of processing practices [29]. The effect of processing can be correlated with the physicochemical parameters of pesticides. The processes acting on pesticide residues in field such as volatilization, hydrolysis, oxidation, metabolism and enzymatic transformation were relevant for reduction of pesticide residues during process.

Effect of some processing methods on the level of organophosphorus residues

pirimiphos-methyl: The data presented in Table (5) and Figure (3) show the effect of some processing techniques on the residual behaviour of pirimiphos-methyl in green bean collected from field (1). It is noted that washing reduced the initial levels to 1.29 ppm (53.60% loss) and to 0.83 ppm (70.30% loss) by cooking of green bean. As well as, cooking of dry bean reduces the residue to 0.28 ppm (89.96% loss) and reduced to 0.96 pm (65.50% loss) in peel.

The data, also indicate that pirimiphos-methyl residues are reduced to 2.50 ppm (63.80 % loss) in potatoes samples collected from field (1) by washing. Both cooking with vinegar 5% and without reduced the pirimiphos-methyl concentration to non detectable level and 1.01 ppm (85.40% loss) and frying process effectively removed pirimiphos-methyl residues from potatoes. This is in agreement with the results previously reported [30]. Also cooking and frying result in removal of pirimiphos-methyl from potatoes, which is in agreement with the work of *Shivankar and Kavadia* [31]. Thus, it may be concluded that potato-tubers treated in such method are suitable for marketing and human consumption.

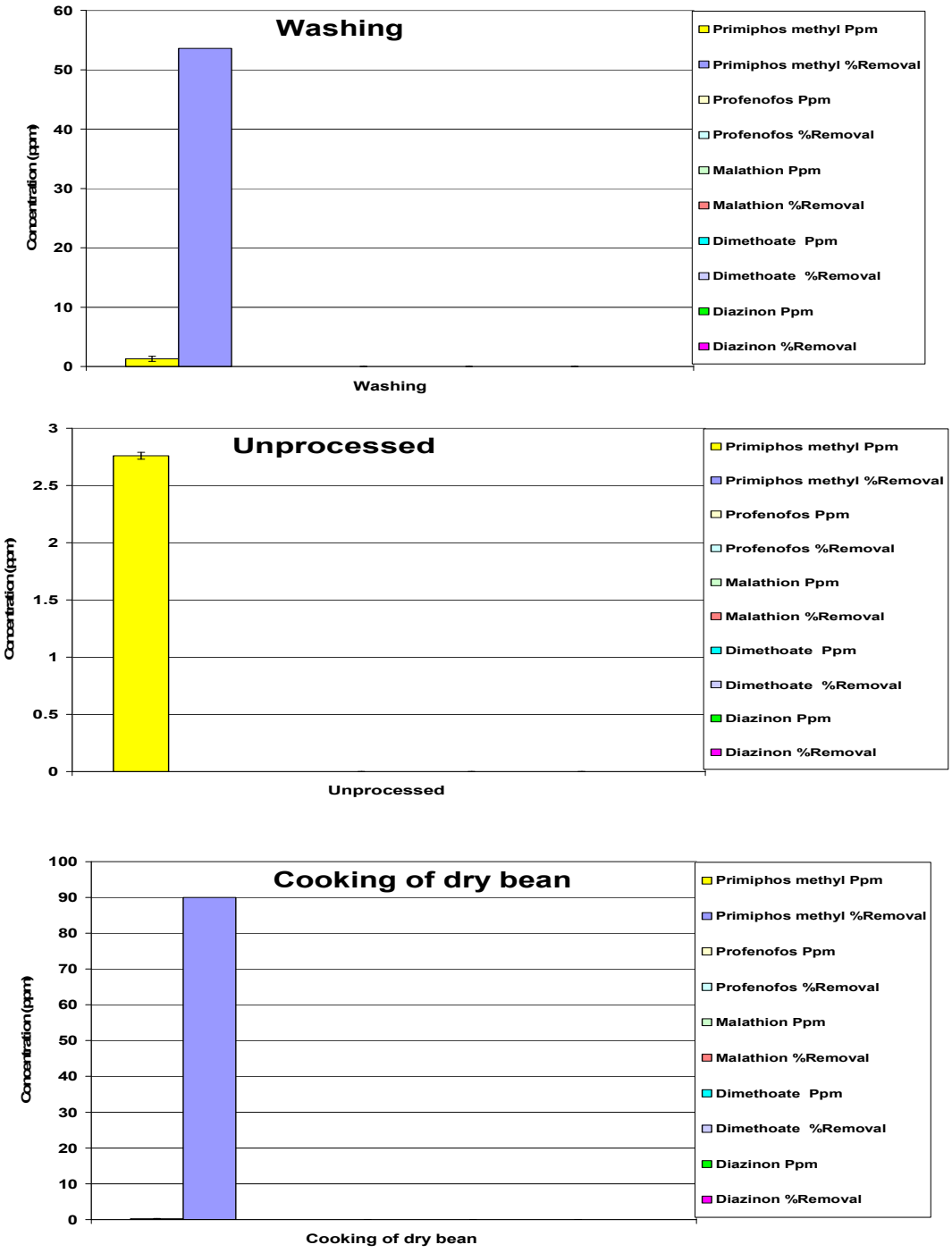


Table 5
Effect of some processing on organophosphorus residues reduction in vegetable samples collected from field 1 and 2

Crops	Process	pirimiphos-methyl		profenofos		malathion		dimethoate		diazinon	
		ppm	% removal	Ppm	% removal	ppm	% removal	ppm	% removal	ppm	% removal
Tomatoes (field 1)	Unprocessed	N.D		0.25	00.00	N.D		N.D		N.D	-
	Washing			0.19	23.30						
	Cooking			N.D	100.0						
Green bean (field 1)	Unprocessed	2.76	00.00	N.D		N.D		N.D		N.D	-
	Washing	1.29	53.60								
	Cooking of green bean	0.83	70.30								
	Cooking of dry bean	0.28	89.96								
	Peel	0.96	65.50								
Potatoes (field 1)	Unprocessed	6.92	00.00	N.D		N.D		N.D		4.98	00.00
	Washing	2.50	63.80							2.25	54.80
	Cooking without vinegar	1.01	85.40							1.05	78.00
	Cooking with vinegar										
	Frying	N.D	100.0							0.78	84.40
		N.D	100.0							N.D	100.0
Potatoes 11-2004 (field 2)	Unprocessed							1.28	00.00		
	Washing							1.10	13.00		
	Cooking without vinegar							N.D	100.0		
	Cooking with vinegar							N.D	100.0		
	frying							N.D	100.0		
Potatoes 2-2005 (field 2)	Unprocessed					0.63	00.0	2.85	00.00		
	Washing					0.53	15.88	1.50	47.00		
	Cooking without vinegar					0.15	76.51	N.D	100.0		
	Cooking with vinegar					N.D	100.0	N.D	-		
	frying					N.D	100.0	N.D	-		

Detection limit of pirimiphos-methyl = 1.5 ppm Detection limit of profenofos = 1 ppm Detection limit of malathion = 1 ppm
N. D = non detectable Detection limit of dimethoate = 5 ppm Detection limit of diazinon = 3 ppm

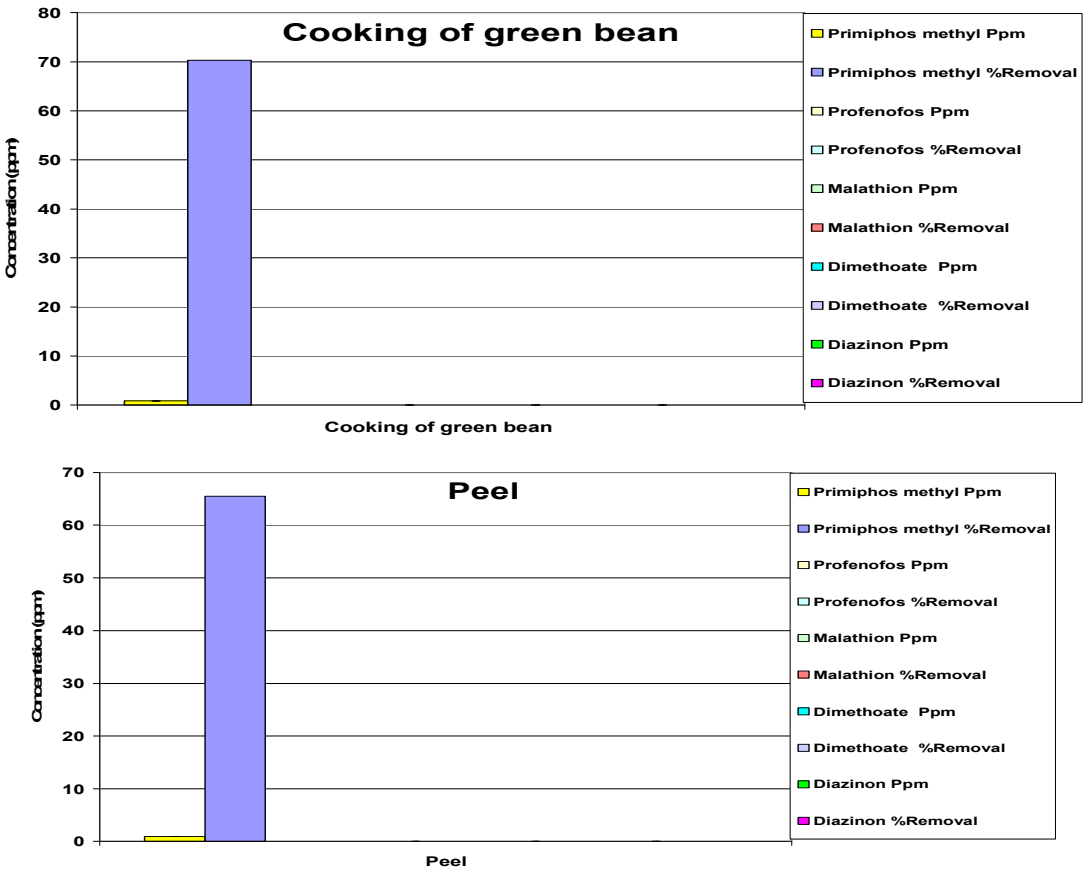
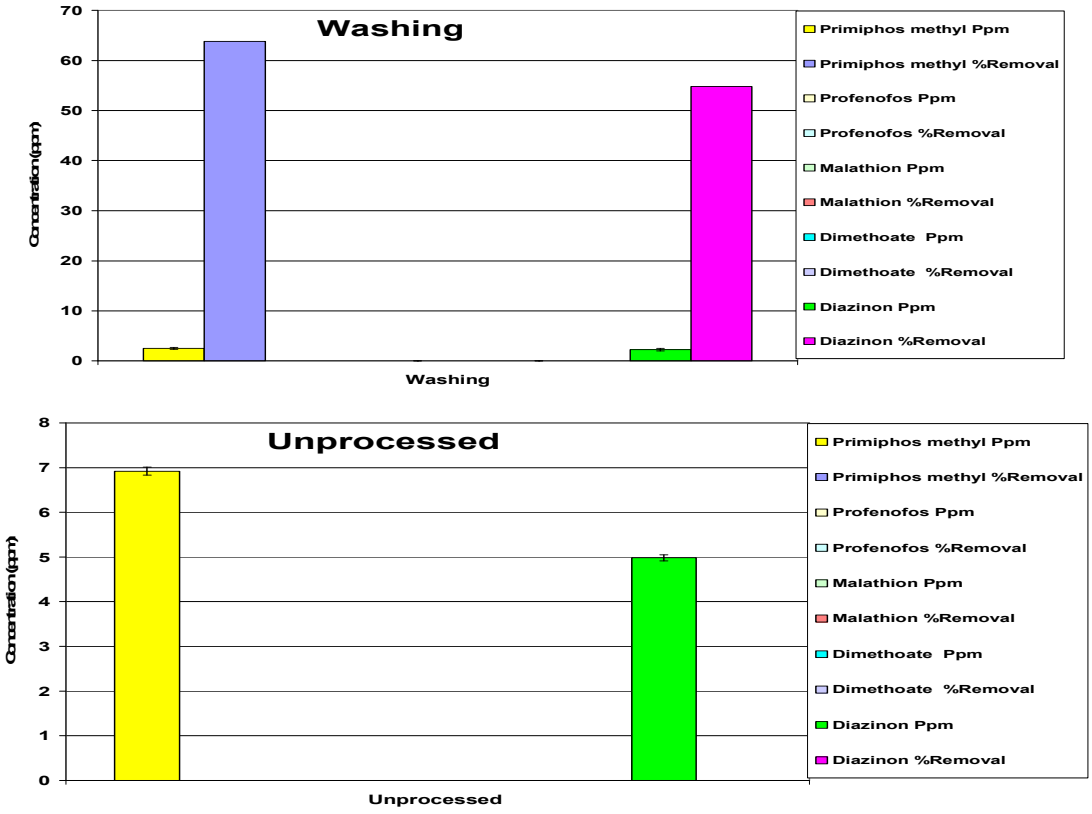


Figure 3: Effect of some processes on organophosphorous residues reduction in green bean samples collected from field 1



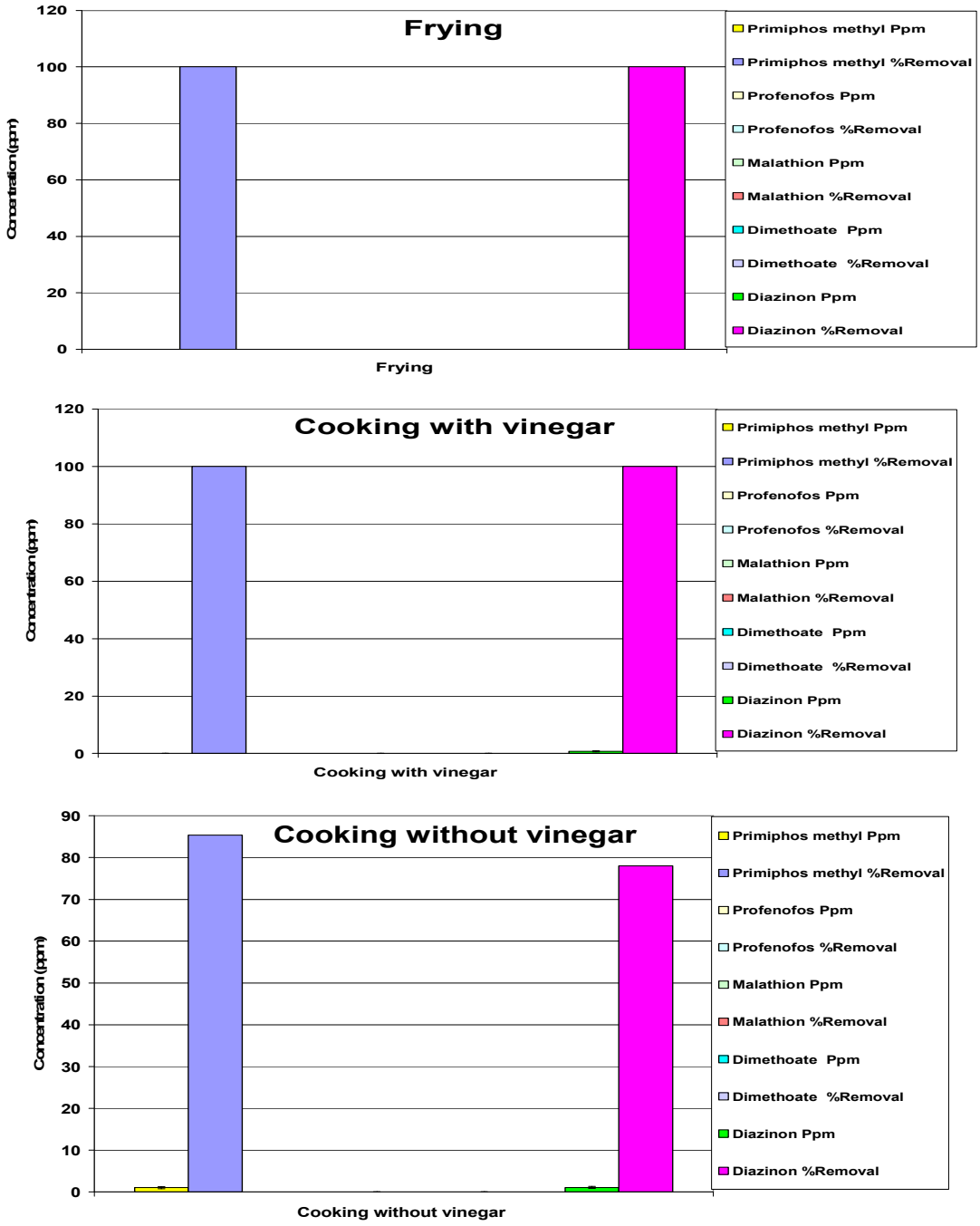


Figure 4: Effect of Some Processes on Organophosphorous Residues Reduction in Potato Samples Collected From Field 1

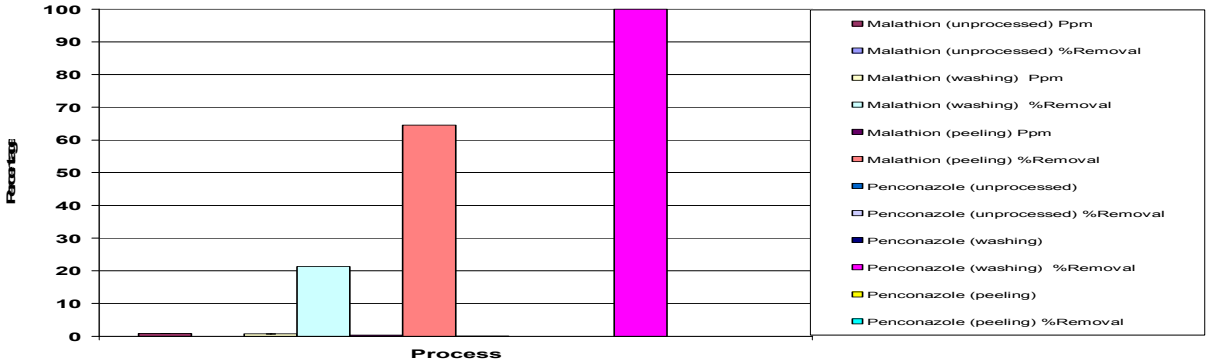


Figure 5: Effect of some processes methods on MT and PCZ in cucumber samples collected from different field 3

Table 6
The effect of different processing methods on carbamates and cypermethrin residues in vegetable samples collected from different fields

Crops \ Pesticides	Process	methomyl		carbofuran		cypermethrin	
		ppm	% removal	ppm	% removal	ppm	% removal
Cucumber (field 3)	Unprocessed	8.17	00.00				
	Washing	6.46	20.94				
	Peeling	3.59	66.00				
Tomatoes (field 2)	Unprocessed	3.23	00.00				
	Washing	2.05	35.94				
	Cooking	0.64	80.22				
Potatoes (field 1)	Unprocessed			0.806	00.00		
	Washing			0.44	45.80		
	Cooking						
	Without vinegar			N.D	100.0		
	Cooking with vinegar			N.D	100.0		
	Frying			0.015	98.16		
Tomatoes (field 1)	Unprocessed					0.32	00.00
	Washing					0.26	19.40
	Cooking					0.16	49.70
Bean (field 1)	Unprocessed					0.48	00.00
	Washing					0.36	25.20
	Cooking green bean					0.17	63.96
	Cooking dry bean					0.105	78.10
	Peel					1.20	-

Detection limit of cypermethrin = 1.5 ng

Profenofos: Table (5) shows that the residue of profenofos in tomatoes collected from field (1) is reduced by 0.19 ppm with a percentage removal of 23.30%. As well, cooking lead to non detectable residue levels of profenofos. Washing the treated tomatoes with tap water decreases the profenofos residues between 22.90 and 12.60% depending on time from pesticide application to fruit harvest. These findings were in agreement with those reported by other authors [23, 32].

Iazinon: The residue of diazinon is found to be reduced to 2.25 ppm (54.80% loss) in potato samples collected from field (1) by washing as given in Table (5) and represented in Figure (4). Both cooking with vinegar 5% and without reduced the diazinon to 0.78 and 1.05 ppm, respectively. Cooking reduces the diazinon concentration to 84.40% as well as, frying caused it to be non detectable. This was in agreement with the results obtained by *Oubina et al* [33].

Malathion: The results listed in Table (5) show that the residual malathion in potato samples from field (2) during February 2005 is reduced by washing to 0.53 ppm (15.88% loss). Both cooking with vinegar 5% and without reduces its concentration to non detectable and 0.15 ppm (76.51% loss) and to non detectable by frying. Data presented in Table (5) and Figure (5) show that the residual malathion levels in cucumber collected from field (3) are reduced to 0.66 ppm (21.30% loss) by washing and further to 0.29 ppm (64.58% loss) by peeling.

Also, it is found that washing processes are found to be efficient in removing organophosphorus insecticides from vegetables.

Dimethoate: The results present in Table (5) indicates that the residue of dimethoate is reduced to 1.10 ppm (13% loss) and 1.50 ppm (47% loss) in potato samples collected from field 2 in November 2004 and February 2005, respectively, by washing. Both cooking with vinegar 5% and without reduced it to non detectable level. As well as, frying causes it to be non detectable in both November 2004 and February 2005. During cooking process, the pesticides residue in the crop is decreased. Some residual pesticides are translocated into the cooking water from the raw materials according to the water solubility expression. The inclination of the regression expression was similar with the same cooking processes and increases with cooking time.

These results were in agreement with the results previously obtained [34, 35] which reported that peeling, boiling and frying of potato-tubers resulted in complete removal of profenofos and malathion residues. Also washing process removed 33.30 and 22.20 % from malathion and fenitrothion residues on cucumber fruits.

Effect of some processing methods on the level of carbamates

Methomyl: Data presented in Table (6) records the residue of methomyl in cucumber samples collected from field 3. It is found that its residue is reduced to 6.46 ppm (20.94% loss) by washing and to 3.59 ppm (66.00% loss) by peeling.

Carbofuran: Data presented in Table (6) show the residual behaviour of carbofuran in potatoes collected from field (1). It is obvious from the data that the concentration of carbofuran is reduced to 0.44 ppm (45.80% loss) by washing. Both cooking with vinegar 5% and without reduced it to non detectable upon cooking. In addition frying reduces the residue to 0.015 ppm (98.17% loss).

Effect of some processing methods on the level of cypermethrin: The effect of some processing on the residual behaviour of cypermethrin in tomatoes collected from field (1) is studied and the data obtained are presented in Table (6). It is noted that washing reduced the initial levels to 0.26 ppm for percentage removal of 19.40%, as well as cooking to 0.16 ppm for percentage removal of 49.70%. The residue of cypermethrin in green bean collected from field (1) is reduced by washing process to 0.36 ppm for a percentage removal of 25.20%. As well, cooking of green bean reduces it to 0.17 ppm for a percentage removal of 63.90%. In addition, the data show that its residue in white bean collected from the same field is reduced by cooking to 0.105 ppm (78.10% loss) and peel is containing 1.20 ppm. Thus, it may be concluded that its residue is mainly located (as nonsystemic pesticide) on the surface of fruit or peel. These results agreed with the findings reported by *Takahashi et al* [36]. He found that heating of cypermethrin aqueous solution at 100 °C caused the concentration of the pesticide to decrease over time scale relevant to food processing.

The data show also that, its residues in tomato samples collected from field (2) is reduced to 2.05 ppm (35.94% loss) by washing and to 0.64 ppm (80.22% loss) by cooking. Similar findings were obtained by many investigators [18].

Effect of some processing methods on the level of organochlorine (dicofol)

Table (7) and Figure (6) report that the residues of dicofol are reduced to 3.36 ppm (60.10% loss) in cucumber collected from field (1) by washing and to 1.34 ppm (84.10% loss) by peeling. However, the effect of washing process on tomatoes collected from field (1) reduces the dicofol residues to 1.96 ppm for 65.00% removal and to 0.98 ppm (82.50% loss) after cooking. These findings were in agreement with those obtained and reported previously [37]. They found that processing were efficient in removing it from vegetables. While, it was disagreed with the finding of Ribeiro et al [38], who mentioned that washing did not allow removal of dicofol residues from vegetables peel.

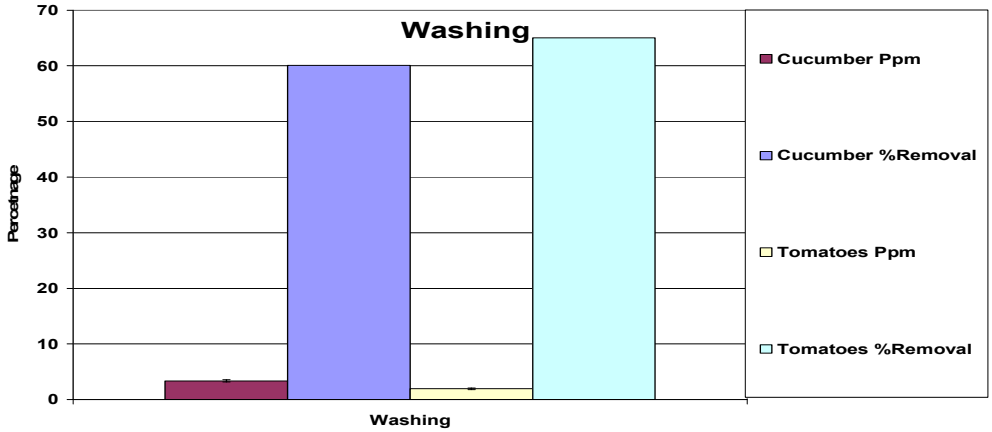


Table 7
Removal of organochlorine, malathion, penconazole and abamectin residues from vegetables

Pesticide / Samples	Process	Dicofol		Malathion		Penconazole		Abamectin	
		ppm	% removal	ppm	% removal	ppm	% removal	ppm	% removal
Cucumber (field 1)	Unprocessed	8.42	00.00						
	Washing	3.36	60.10						
	Peeling	1.34	84.10						
Tomatoes (field 1)	Unprocessed	5.60	00.00						
	Washing	1.96	65.00						
	Cooking	0.98	82.50						
Cucumber (field 3)	Unprocessed			0.83	00.00	0.082	00.00		
	Washing			0.66	21.30	N.D	100.0		
	Peeling			0.29	64.58				
Cucumber Field (1)	Unprocessed							12.168	00.00
	Washing							4.87	60.00
	peeling							2.07	83.00
Tomatoes Field (1)	Unprocessed							1.40	00.0
	Washing							0.35	75.00
	Cooking							N.D	100.0
Tomatoes Field (2)	Unprocessed							10.52	00.00
	Washing							8.60	18.00
	Cooking							5.91	43.70

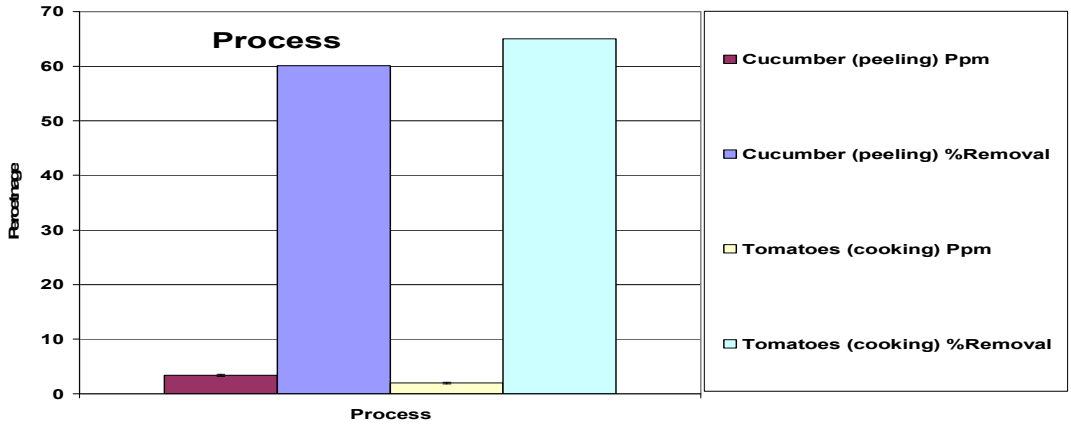


Figure 6: Removal of DCF residue from vegetable samples collected from field 1

Effect of some processing methods on level of penconazole (fungicide) : The data in Table (7) reveal that the penconazole is non detectable in cucumber samples collected from field 3 after washing and peeling. This is in agreement with the findings of Gennari et al [39] as they indicate that similar processing procedures had varied effect on reducing or removing pesticide residues originally present on or in mature fresh leaves or fruits of the different cultivars.

Effect of some processing methods on level of abamectin: Data presented in Table (7) record the residue of abamectin in cucumber samples from field (1). It is found that, the concentration of abamectin is reduced to 4.87 ppm (60.0% loss) by washing and to 2.07 ppm (83.0% loss). While, the initial deposits of abamectin in tomato samples collected from field (1) is reduced to 0.35 ppm (75.0% loss) by washing and to nondetectable by cooking. However abamectin in tomato samples collected from field 2 is reduced to 5.91 ppm (43.70% loss). Thus, it can be concluded that the combined washing and peeling processes may remove > 75.0% of abamectin from cucumber. The values of SD and RSD obtained for three replicates are found to be less than 3% which indicates the reproducibility of the proposed methods.

Persistence of pesticide residues in tested water : onitoring of pesticide residues were conducted at different locations in Egypt. Drainage water and irrigation water samples were collected from different locations. The residues of pesticides varied between different locations. The data obtained show that the concentrations of malathion in irrigation water and drainage water samples collected from field (1) are found to be 4.43 and 4.26 ppm,

respectively. While, malathion concentration in irrigation and drainage water collected from field (2) is found to be 2.76 and 16.67 ppm, respectively. Also, the data reported indicate that the concentration of malathion is found to be 3.04 ppm in irrigation water (well) samples collected from field (3). Also the concentration of dimethoate is found to be 13.80 ppm in drainage water samples collected from field (2). Also, concentrations of methomyl and aldicarb in drainage water samples collected from field (1) are 2.60 and 1.76 ppm, respectively. While, concentration of methomyl is 2.70 ppm in irrigation water and concentration of aldicarb is 1.84 ppm in drainage water sample collected from field (2). Meanwhile, the concentration of dicofol in drainage water is 1.60 ppm in field 1 and the concentration of abamectin is 3.20 ppm in irrigation water collected from field (1). The MRL's for malathion and methomyl in water (Table 3) were 0.01 and 0.05 ppm, respectively. Therefore, the residue of these pesticides in water was higher than their corresponding MRL's. These results agreed with those previously reported [40].

The effect of storage on abamectin residues

Results obtained for the residual behaviour of abamectin in cucumber, green bean, dry bean, peel, soil, irrigation water and drainage water samples collected from El-Khatab village Dakahlia governorate, governorates, Egypt at June 2005, indicate that the initial deposits are 6.42, 16.08, 10.94, 9.83, 4.50, 3.20 ppm and non detectable, respectively, after spraying for one day. Three days later, the residues are reduced to 3.01, 7.66, 5.45, 4.77 and 2.26 ppm, respectively. After seven days, the initial deposits of abamectin are reduced to1.99, 2.84, 1.71, 2.04 and 1.04 ppm, respectively.

Conclusion

Monitoring of pesticides in different fields

Water, soil and plant samples were examined for organophosphorus, carbamates, organochlorine, triazole, pyrethroid, neonicotinoid and vermectin pesticides. Residue of pirimiphos-methyl in green bean and potatoes were found to be higher than their corresponding MRL's (0.50 and 0.05 ppm, respectively) indicating that it required a longer post harvest period before consumption. Potatoes contained the highest levels of dimethoate and diazinon as organophosphorus pesticides. Residue of methomyl (carbamate) in cucumber and tomatoes were higher than their corresponding MRL's, (0.20 and 0.5 ppm, respectively). Aldicarb was found in soil and irrigation water in field (1). Dicofol as organochlorine pesticides was detected in tested samples. Residue of dicofol in cucumber and tomatoes samples was higher than their corresponding MRL's (2.00 and 1.00 ppm, respectively). Thus, dicofol was the most persistent and found to persist in field crop grown in soils for long period of time. Cypermethrin residues in tomatoes and green bean were found to be lower than their corresponding MRL's (0.50 and 0.50 ppm, respectively). Residues of abamectin in cucumber and tomatoes were higher than MRL's (0.001 and 0.001 ppm, respectively) indicating that it required a longer post harvest period before consumption. It was found also that, washing process eliminated approximately 13-60% of organophosphorus, 20-50% of carbamates, 19-25% of cypermethrin, 60% of dicofol, 100% of penconazole and 18-75% of abamectin residues. Peeling of washed cucumber removed 65% of malathion, 66% of methomyl, 80% of dicofol and 83% of abamectin. The most effective process applied was peeling specially with cucumber as it had the highest effect in decreasing residue associated with the plant. Thermal processes i.e. cooking of tomatoes, potatoes and green bean, resulted in 70-100 % residues removal of organophosphorus, as well as removal of 80-100% of the carbamate 50-100% of cypermethrin, more than 80% of dicofol and 43-100% of abamectin.

It was noticed that cooking of dry bean resulted in elimination of pesticides more than cooking of green bean. While potatoes with vinegar 5% eliminated pesticide residues more than cooking without vinegar. On the other hand, pesticides were eliminated more by cooking in acidic media. Frying, also lead to non detectable residues in vegetables. Thus, it might be concluded that a combination of simple washing and peeling removed 10 to 85 % of metals and insecticides if applied before consumption. As well, cooking and frying might help to remove 25-100 % of the residual metals and insecticides. The results indicate that the initial deposits of residue gradually decreased with storage time. However, they were not completely eliminated during storage periods.

Recommendations

- Monitoring programmes of pesticide residues in local produces must be expanded to include all food items and potentially harmful pesticide residues in order to generate information and establishing data based on food contaminants. Thus, enabling the follow up of pesticide use and to take corrective action in order to minimize their residues.
- Washing as a preliminary preparation step should be emphasized and recommended for consumers by packing companies for vegetables and fruits.
- The importance of peeling has to be recognized as a means for improving the quality assurance and decontamination of some stored products. As well, the peel can be used as an indicator of residue contamination/ decontamination of produce.
- Reduce pesticide used by developing other alternative methods such as integrated pest management (IPM) and sustainable organic agriculture. The use of preparation pesticide should always be reviewed by the ministry and affiliate cooperatives in order to ensure no incidents or misuse or negligence reoccurs.

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